Mutually exclusive cohesive and adhesive properties in the failure of thin coatings in sliding mode

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ABSTRACT

Scratch tests were done on Si-C-N coatings developed on Si (100) substrates useful for MEMS devices in unconducive environments. The interfacial adhesive strength got manifested in different failure morphologies. The features depicting their chronological failures were analyzed by relating the load-scratch length plots with the scratch track image. The cohesive and adhesive strength were found to be independent to each other with each of them getting manifested in different ways.

Keywords: Scratch, hard coatings, Si-C-N, cohesion, adhesion

INTRODUCTION

Silicon-Carbon-Nitride (Si-C-N) coatings having multiphases, are popular for their enhanced fracture resistance are used in micro-electro-mechanical-system devices in aerospace **[1-3]**. Static indentation has been used to assess the fracture toughness of these coatings **[4]**. Sliding indentations in comparison are less addressed **[5-8]** are therefore has been presented herein detail. The coating being subject to a ramping load while sliding depicts the strength profile with respect to its thickness. The nature of failure has been found to depend on the relative coating-substrate hardness, scratch velocity, and the loading rate as reported earlier for nano scratch tests **[9]**. However, the study of thin coatings subject to higher loads at micro level is more intriguing considering the use of hard coatings as a protective coating.

MATERIALS & METHODS

Si-C-N coatings were deposited on Si (100) substrates by magnetron sputtering (HHV, Bangalore, India) in Ar/N_2 atmosphere from SiC target. The sliding indents were carried out by Scratch Test Tr-101 (Ducom, Bangalore, India) that used a Rockwell C indenter at a speed of **0.2 mm/s** at different loading rates.

RESULTS & DISCUSSIONS

Better adhesion in terms of critical load and failure nature has been observed in case of coatings on silicon substrates compared to that of steel substrates **[10]**. The interfacial shear stress generated at the coating–substrate interface plays a major role in the adhesion properties. **Fig 1-5** shows the different scratch tests performed on Si-C-N coatings deposited on silicon substrates.

The failures taking place in thin coatings in sliding mode cannot be solely represented by a critical load (**Lc**) corresponding to a single phenomenon of failure. During the scratching even, there may be multiple instances where localized coating failure may take place before showing a total breakdown at a load which is usually called the **Lc**. The scratch plot shown in **Fig 1a** with the image of the scratch track (**Fig 1b**) shows more than one places where the coating has undergone a breakdown. Profiles of the marked regions in the scratch track are given in **Fig 1(c-f)**.

The indenter started scratching the coating surface from a load of **5 N** and got a proportional increase in tractional force (**F_T**) till it was able to dig into the coating for a load of **10 N** at **0.5 mm**. This resulted in decrease in F_T. The cross-sectional profile clearly shows the indenter penetration and formation of radial cracks thereafter (**Fig 1c**). The cracks became wider as the slide progressed (**Fig 1 d, e**) and the distribution was matched with a polynomial as shown in **eq1**. The negative coefficient are representative of the crack depths while the positive one are related to their frequency per unit length.

Further scratching caused tensile cracks indicative of strong adhesion for films deposited at deposition temperatures (~500 ^{o}C) at a power of 400 W and pressure of 1 Pa in Ar and nitrogen atmosphere. The cracking phenomenon was confined within the scratch only. These semicircular trajectories of cracks parallel to the trailing edge of the indenter arise due to tensile frictional force present behind the stylus and balance the compressive frictional force ahead.

At about **1mm**, severe plastic deformation and *lateral* cracks got developed sideways of the scratch track as shown in the track image. Radial cracks also were seen. The **F_T** values showed ups and downs corresponding to the multiple failures till **2 mm**. The coating experienced major failure between **21 to 26 N** involving a plastic overflow where the coating is pushed into the substrate and delamination (chipping) of the coatings also occurs. The cross-sectional profiles of the failed regions are shown in **Fig 1(e, f)**.

For a lower loading rate of **5N/mm**, the scratch track features were similar with appearance of Tensile cracks as a reflection of cohesive through thickness failure once the indenter was able to cause an initial penetration at 0.5mm for a load of 5N, which also caused a sudden jump in $F_{T,}$ The cracks were confined inside the scratch track till about **1 mm** where radial cracks were seen to emerge at a load of **10N**. The radial cracks were seen till **1.5 mm** accompanied by an increase in F_T at **15N** (**Fig 2a**). The COF plot given in **Fig 2b** clearly shows the three regions of the three distinct regions of the track. Lateral cracks were seen thereafter arising symmetrically from both the sides (**Fig 2c**).

The round flakes that emerged from the side of the scratch trajectory, which is also a sign of plastic deformation of the film and the substrate, show that coating removal by buckling of the film at higher weights happened. The fourth root of toughness has an inverse relationship with spall extent. Before the indenter, a roughly trapezoidal area of the film delaminates and spalls. The indenter's in-plane compressive stress causes the delamination, which thereafter happens. The delamination crack will be forced into the substrate. Therefore, the delamination fracture gets contained to the plane of the interface provided the interfacial toughness is significantly lower than the substrate's toughness [11].

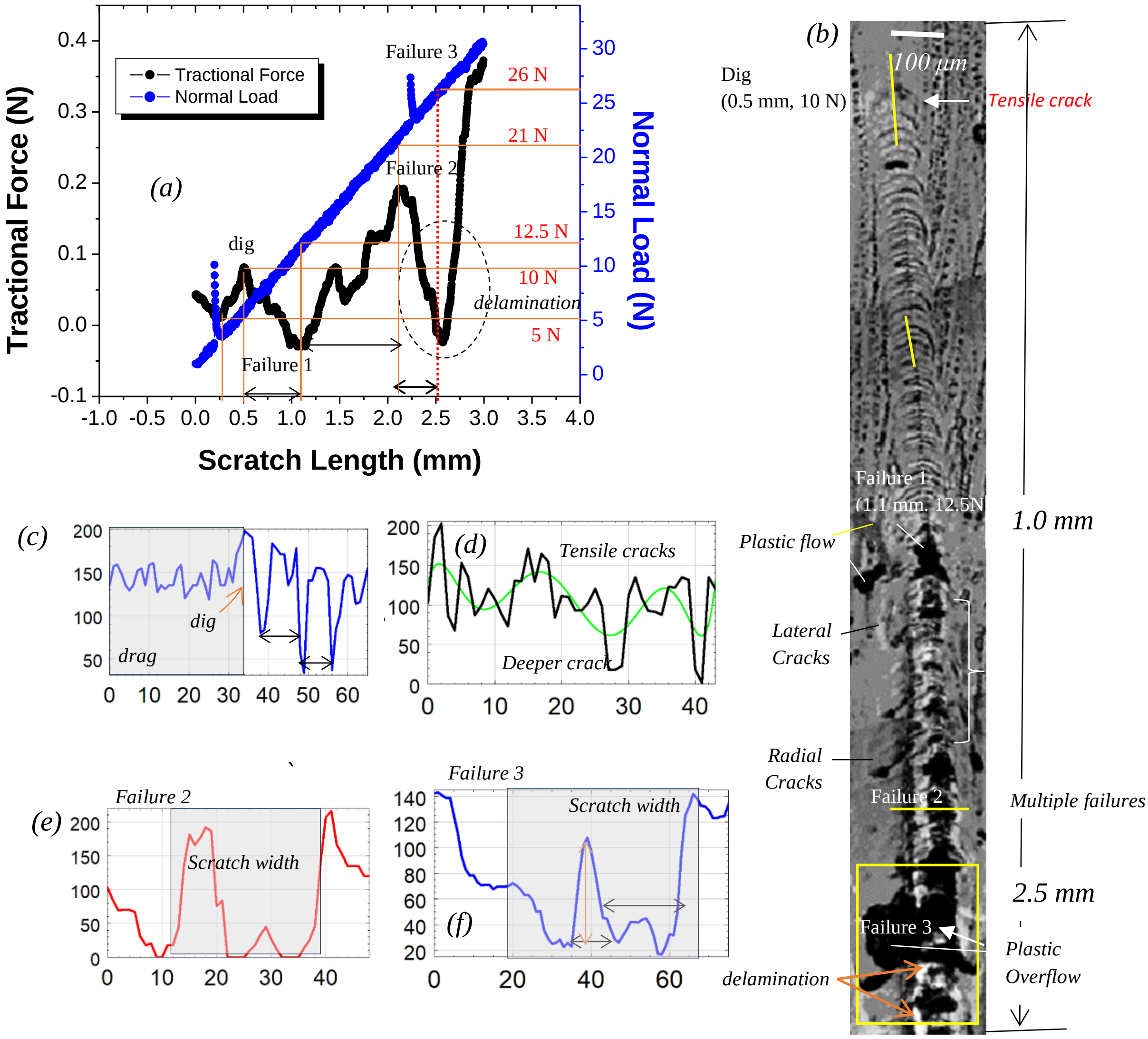

Fig 1: Tensile cracking and flaking during scratching with **10N/mm** loading rate for Si-C-N coated silicon substrates showing plots of (a) Normal load and Tractional force vs. stroke length, (b)C.O. F & normal load vs. scratch length and (c)the optical micrograph of the scratch track (reproduced with permission [6]) (e, f) cross-sectional profiles of different failed regions

Formula: $y = a+bx+cx^2+dx^3+ex^4+fx^5+gx^6+hx^7+ix^8$ **(1)**

a = 128.59681; b = 31.23122; c = -12.83063; d = 1.57894; e = -0.072949; f = 0.00044654; g = 6.42950E-5; h = -1.87802E-6; i = 1.57979E-8

For coatings having lower thickness, through tensile cracks were absent after initial penetration. The initial responsive tractional force (F_T) increase with ramping normal load (FN) is also not observed. The coating shows a sudden brittle failure as can be observed at a sliding distance of **1.8m** (*l*) at a load of **18.5 N** (Lc) (Fig 3a). The events get clearly depicted in the

COF plots with adhesive failure occurring till a load of **20 N** **(Fig 3b)** for a COF of 0.042. The adhesive was brittle in nature with absence of any plastic flow as observed in the previous cases **(Fig 3c)**. There were also no lateral and radial cracks indicating lower cohesive strength. The cross-sectional linear profile of the scratch track before failure shows a groove of area (height ×width) of 240 μm^2 (**Fig 3d**). The material loss after adhesive failure is 800 μm^2 (**Fig 3e**). The specific wear rate WR_s is given as **eq 1a**, which is equivalent to **eq 2b** where ***l*** is the corresponding scratch length at which the material loss is being considered, and t is the coating thickness (0.5 μm). The value comes out as **1.6 mm^2/N**

$$WR_s = \frac{Volume\ Loss}{Load\ .\ sliding\ distance} \quad \textbf{(2a)}$$

$$WR_s = \frac{(hw)\ l}{L_c\ t} \quad \textbf{(2b)}$$

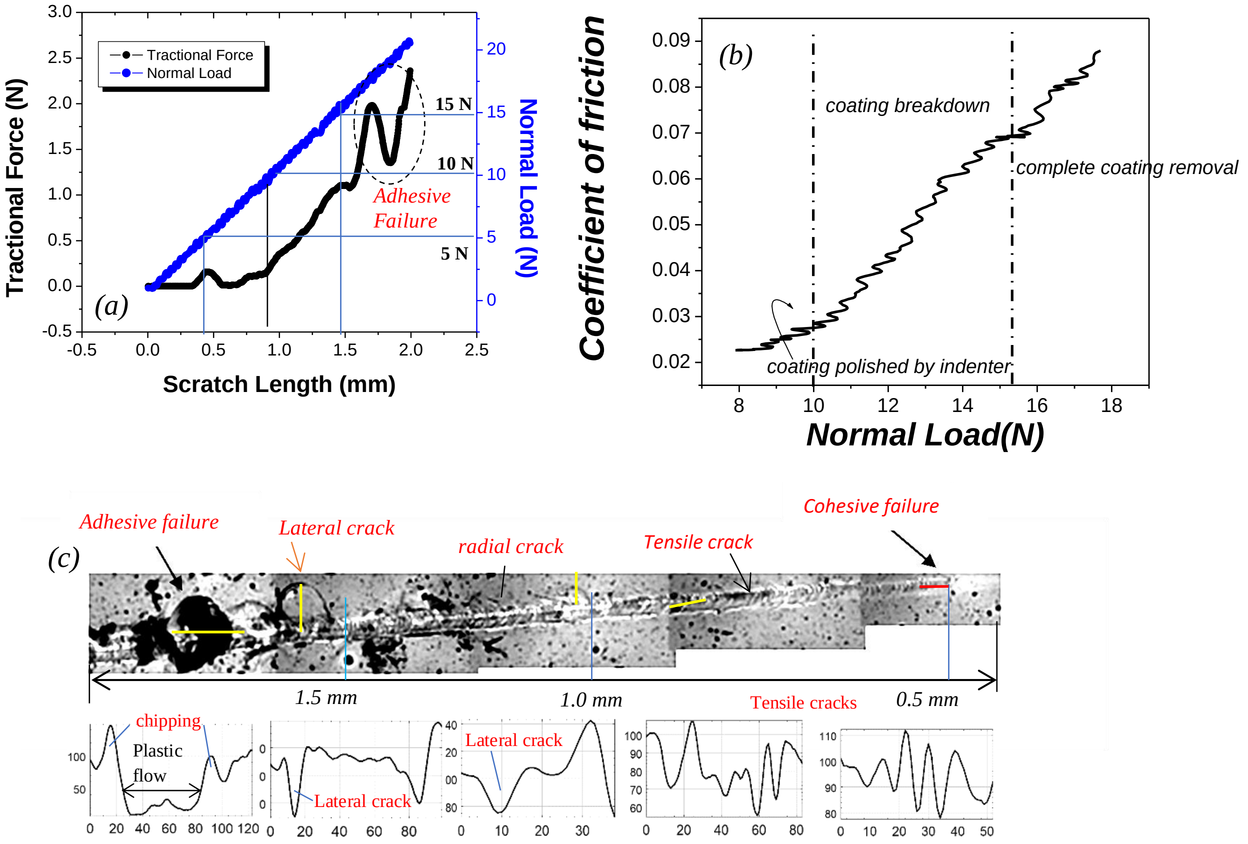

Fig 2. Scratch tests with **5N/mm** loading rate for silicon substrates showing plots of (a) Normal load and Tractional force vs. stroke length, (b) C.O.F vs. normal load and (c) the optical micrograph of the scratch track showing failure of the film at **15 N** and profiles of the marked regions (reproduced with permission **[6]**).

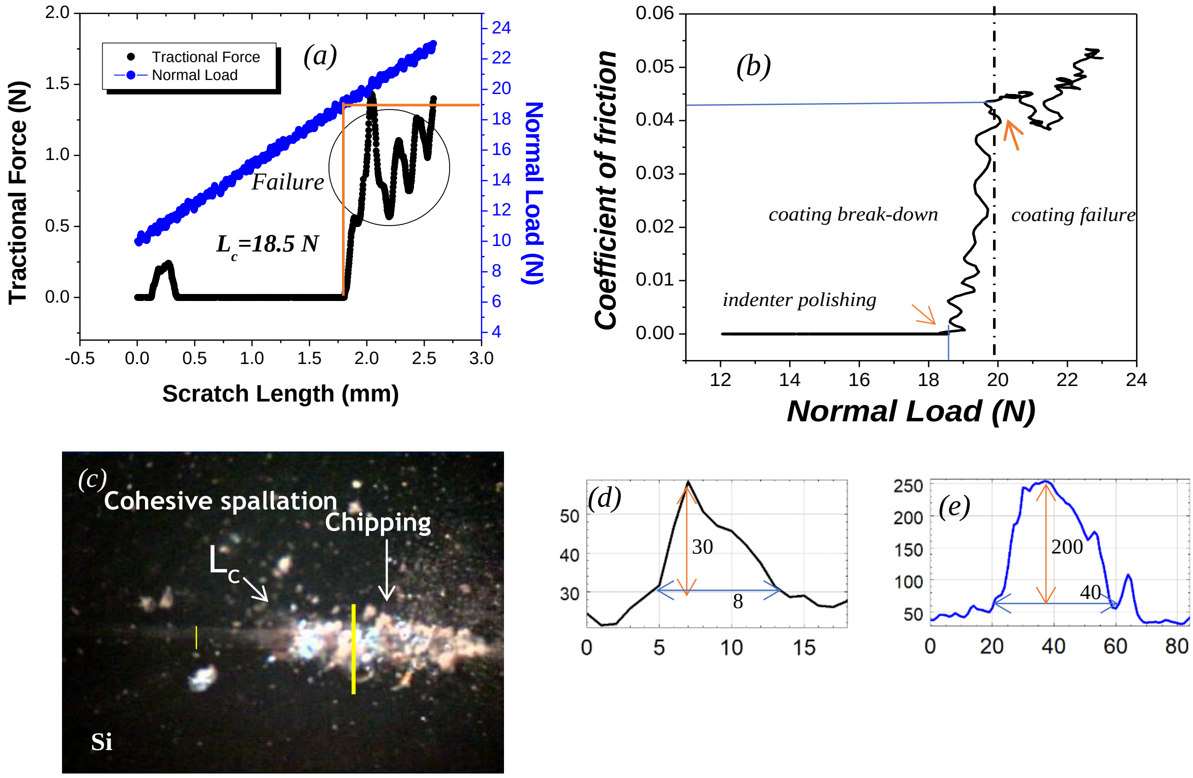

Fig 3: Scratch tests with 5N/mm loading rate for silicon substrates showing plots of (a) Normal load and Tractional force vs. stroke length, (b) C.O.F vs. normal load and (c)the optical micrograph of the scratch track showing failure of the film at **18.5** N by cohesive spallation and chipping (reproduced with permission **[6]**). Cross-sectional profiles of the (d) scratch groove before failure and (e) region after adhesive failure.

CONCLUSIONS

Si-C-N coatings deposited on Si(100) substrates with good cohesion showed semicircular through thickness tensile cracks followed by radial and radial cracks and ultimately causing an adhesive failure. The adhesive failure was found to consist of highly plastic flow region along with coating delamination. Coatings having lower thickness and cohesive strength showed no through thickness tensile cracks. Even though the adhesion was high (**higher Lc**) and the adhesive failure was also brittle in nature with a high wear rate of **1.6 mm^2/N**. The cohesive and adhesive properties are therefore mutually exclusive properties.

REFERENCE

1. Tomastik, J.; Ctvrtlik, R.; Ingr, T.; Manak, J.; Opletalova, A. Effect of Nitrogen Doping and Temperature on Mechanical Durability of Silicon Carbide Thin Films. Sci. Rep. 2018, 8 (1). https://doi.org/10.1038/s41598-018-28704-3.
2. A S. Bhattacharyya, Arnab; P. Kumar, Ramgiri; Acharya, Gaurav; Ranjan, Vivek, Current Smart Materials, 2, 1, 2017, pp. 39-43https://doi.org/10.2174/2405465801666161130154515
3. Mishra, S. K.; Bhattacharyya, A. S.; Rupa, P. K. P.; Pathak, L. C. Nanoscience and Nanotechnology Letters, 4, 3, 2012, 352-357(6) https://doi.org/10.1166/nnl.2012.1320
4. Chen, J. (2012). Indentation-based methods to assess fracture toughness for thin coatings. *Journal of Physics D: Applied Physics*, *45*(20), 203001.
5. A.S. Bhattacharyya, G.C. Das, S. Mukherjee, S.K. Mishra, Effect of radio frequency and direct current modes of deposition on protective metallurgical hard silicon carbon nitride coatings by magnetron sputtering, *Vacuum*,83, 12, 2009, 1464-1469, https://doi.org/10.1016/j.vacuum.2009.06.051.
6. Mishra, S. K.; Bhattacharyya, A. S. Adhesion and Indentation Fracture Behavior of Silicon Carbonitride Nanocomposite Coatings Deposited by Magnetron Sputtering. In Silicon-based Nanomaterials; Springer New York: New York, NY, 2013; pp 215–241.
7. Mishra, Suman K., and A. S. Bhattacharyya. "Effect of substrate temperature on the adhesion properties of magnetron sputtered nano-composite Si–C–N hard thin films." Materials Letters 62, no. 3 (2008): 398-402.
8. S.K. Mishra, A.S. Bhattacharyya, P. Mahato, L.C. Pathak, Multicomponent TiSiBC superhard and tough composite coatings by magnetron sputtering, Surface and Coatings Technology, 207, 2012,19-23, https://doi.org/10.1016/j.surfcoat.2012.03.047.
9. A.S. Bhattacharyya. Sliding indentation: Failure modes with study of velocity and loading rate, Surface Topography: Metrology and Properties 2021 *Surf. Topogr.: Metrol. Prop.* 9 (2021) 035052 https://doi.org/10.1088/2051-672X/ac28aa
10. A S Bhattacharyya. Dual mode fracture based on loading rate during sliding indentation of Si-C-N hard coatings on 304S substrates. *Authorea.* October 19, 2023. 10.22541/au.169774192.22359266/v1
11. R. Dash, K. Bhattacharyya, A.S. Bhattacharyya, Film failure at earlier and later stages of nanoindentation in static and sliding mode. *Eng Fail Anal* (2023) 150, 107353 https://doi.org/10.1016/j.engfailanal.2023.107353